MOLECULAR MODELLING OF KEROGENS AND RELATED COMPOUNDS AS A TOOL FOR PREDICTION OF FOSSIL FUELS GENESIS

F. BEHAR*, M. VANDENBROUCKE* and J. L. FAULON**
* IFP, 1-4 Avenue Bois Préau, 92506 RUEIL MALMAISON, FRANCE. ** C.A.O. Robotique, Armines, 60 Boulevard St Michel,75272 PARIS Cedex 06, FRANCE

INTRODUCTION

Kerogen is defined as that fraction of sedimentary organic matter which is insoluble in usual organic solvents (1). It is a mixture of macromolecules whose structures evolve under the influence of time and temperature due to increasing sediment burial. Thermal cracking of kerogen (primary cracking) will lead to petroleum generation. Oil is formed first, further thermal degradation of kerogen and oil (secondary cracking) will produce gaseous compounds. Prediction of both quantity and quality of hydrocarbons generated from a given kerogen buried in a given sedimentary basin are of paramount importance as exploration guide. Thus, simulation of thermal degradation of organic matter in laboratory has been performed in order to elaborate kinetic models. These kinetic models can be really predictive only when the three following conditions are fulfilled:

1°) knowledge of chemical structure of reactants,

2°) knowledge of chemical structure of degradation products,

3°) establishment of laws relating chemical structures of reactants and products.

For many years, attention has been focused on characterization of pyrolysis products and establishment of kinetic laws, but a chemical structure was not available when kerogen, coal or heavy ends of petroleum such as resins and asphaltenes were studied. In this paper, we will present the approach we are following for modelling these complex structures and how we can relate kerogen and/or asphaltenes modelling to kinetics.

Many experimental devices have been developed for simulating thermal cracking of kerogen or asphaltenes (2). As these insoluble compounds are generally not vaporisable, experimental simulation of cracking can be done either in open pyrolysis systems swept by an inert carrier gas (3, 4, 5 among others) or in closed pyrolysis systems (6, 7 among others). An open pyrolysis system is very convenient because it allows continuous detection of effluents and programmed temperature increase. Thus, many samples can be studied in a short experimentation time. Nevertheless, transport effects due to the delay between formation and detection of effluents, can both modify kinetic parameters such as the apparent activation energies (8) and underestimate the yield of heavy compounds such as resins and asphaltenes; these latter, if they are only partially swept out of the pyrolysis chamber, can be further cracked together with the residual kerogen. Moreover, secondary cracking reactions cannot be simulated as pyrolysis products are swept away as soon as they are generated. In a closed pyrolysis system, primary cracking can be observed for low conversion yields, whereas secondary cracking will occur for higher severity, but care must be taken regarding both wall effects (9) and overlap of primary and secondary reactions. There are currently not enough available data for doing a real comparison between

open and closed systems. As the aim of our work is to elaborate a complete kinetic scheme including both primary and secondary cracking, we have chosen to perform the experimental work in a closed system.

Compounds involved in thermal cracking reactions can be identified unambiguously when present either as gaseous or liquid products. Therefore, they can be classified according to their chemical structure and carbon number, and their relative thermal stabilities can be compared.

When kerogen and heavy ends of petroleum are pyrolysed, characterization of these latter in terms of chemical bonds distribution and molecular moieties is not available. As a consequence, establishment of a predictive kinetic scheme based on chemical structure for these complex macromolecules, is not yet possible. To overcome this difficulty, we propose to use the molecular modelling software Xmol (10) which, through a combination of atomic and molecular analyses of an unknown insoluble sedimentary organic matter, builds up a self consistent 3D chemical structure. Although the 3D structural representation can be disputed, and is maybe unrealistic, it allows a correct statistical balance of all kinds of bonds present in the macromolecule. Thus, the amount and the distribution of these chemical bonds can be listed and can be related to the distribution of stoichiometric coefficients of the kinetic scheme obtained from experimental simulation.

In this paper, preliminary experimental results on kinetics of cracking of oils and kerogens will be presented. We are currently gathering all the data necessary to link kinetic scheme and molecular structure of reference kerogens.

SAMPLES

Four samples were selected: two kerogens (Type II and Type III) and two oils (Boscan and Pematang), the first one being aromatic and the second one paraffinic. As during thermal cracking each oil produces both lighter and heavier molecules than those present in the initial oil, the resulting pyrolysate will be a complex mixture of new compounds plus reactants not yet degraded. In order to discriminate between reactants and products, we have chosen to study each oil after fractionation into two classes: the first one (distillate) comprising light hydrocarbons ranging from C6 to C16, the second one (topped residue) comprising both hydrocarbons (saturates + aromatics) and polar compounds (resins + asphaltenes). Chemical composition and elemental analysis of the initial samples are reported in tables 1 and 2. .

EXPERIMENTAL SIMULATION

The experiments were carried out in sealed gold tubes under pressure; pyrolysis conditions are listed in table 3.

Pyrolysis products were analyzed according to the following procedure (11):
- non hydrocarbon gases:
    * quantification of individual species such as H20, CO2 and H2S,
    * atomic balance for carbon, hydrogen, oxygen and sulfur.
- C1-C5 fraction:
    * identification and quantification of all hydrocarbons,
    * carbon and hydrogen balances.
- C6-C13 fraction:

* separation of saturates plus unsaturates and aromatics,
* quantification of all saturates,
* quantification and identification of nearly all aromatics,
* carbon and hydrogen balances.
- C14+ extract:
* separation into saturates, aromatics and NSO compounds and quantification,
* elemental analysis of total C14+ fraction
. - insoluble residue:
* quantification and elemental analysis.

Consequently, atomic balances are done on the total pyrolysis products recovered in each experiment in order to be compared to the elemental analysis of the initial sample. This allows a check of the experimental data independent of the mass balance. Table 4 presents an example of a set of experimental data obtained at 300[C for the Type II kerogen.

Kinetic model for kerogen and oil cracking

Cracking reactions can be described by a set of first order reactions involving the transformation of the initial reactant into new compounds or new chemical classes of compounds, some of them being stable and others unstable in the limits of the experimental domain considered.

A first order reaction obeys the Arrhenius law: $dx/dt = - kx$ where x is the reactant concentration and k, the first order rate constant, is equal to $Ae-E/RT$. The preexponential factor A and the activation energy E are the parameters to be determined by experimental simulation and they are characteristic of each cracking reaction. From our 245 experiments, a general kinetic scheme can be elaborated. It comprises six stable classes, H2O, CO2, H2S, C1, ARO.S (C6-C13 stable aromatics such as benzene, toluene, xylenes and naphthalene) and coke and 7 unstable classes, C2, C3-C5, C6-C13 SAT., C8-C13 ARO., C14+ SAT., ARO.U (unstable C14+ aromatics such as alkyl and/or naphtheno aromatics, resins and asphaltenes), condensed C14+ aromatics (ARO.C) and residual kerogen (RK). In this scheme, 9 cracking reactions are involved: .

1. Kerogen ---> H2O + CO2 + H2S + C14+SAT + ARO.U + RK
2. ARO.U ---> H2O + CO2 + H2S + C14+SAT + C6-C13 SAT + ARO.C + coke
3. ARO.C ---> C1 + C3-C5 + coke
4. C14+SAT ---> C3-C5 + C6-C13 SAT + C8-C13 ARO
5. C6-C13 SAT ---> C1 + C2 + C3-C5 + C8-C13 ARO + ARO.C
6. C8-C13 ARO ---> C1 + ARO.S + ARO.C
7. C3-C5 ---> C1 + C2 + C6-C13 SAT + C8-C13 ARO
8. C2 ---> C1 + C3-C5 + C6-C13 SAT
9. RK ---> C1 + coke

In each reaction, stoichiometric coefficients multiply each compound or class of compounds formed. In order to reduce the number of free parameters to be experimentally determined, the preexponential factor A is assumed to be the same for all cracking reactions. Then, from these experiments, kinetic parameters such as activation energies and stoichiometric coefficients were calculated, through

optimization successively on each kerogen, each topped oil and each distillate, then on each total oil and finally on the two total oils. Consequently, we have a unified kinetic model for oil cracking (reactions 2 to 8), provided the proportions of chemical classes as defined above are known in the initial oil. For kerogen cracking (reactions 1 and 9), due to the complexity of the initial chemical composition of kerogen, a specific kinetic model is currently proposed for each sample.

CHEMICAL MODELLING

Various quantitative analytical techniques allow us to define a macromolecular structure of kerogen or asphaltenes more or less precisely. These techniques can be divided into 2 classes (Table 5). One includes atomic analyses such as elemental analysis, spectroscopic techniques and the quantitative determination of some functional groups. The other involves quantitative analysis of molecular moieties obtained by degradation reactions such as pyrolysis (12, 13, 14), chemical attack (15, 16) or natural thermal cracking during burial of sediments (17). After fractionation, these molecular moieties can be identified and quantified by chromatography or mass spectrometry. Results provide molecular level information because the inference is that the small molecules are component fragments of the larger macromolecule. As these analytical data are not sufficient to allow a detailed representation of a macromolecular structure, some assumptions, have to be made (Table 6). In order to combine all these informations and to elaborate a chemical model, a new chemical representation of molecules labelled "molecular signature" is proposed: each molecule is defined by a series of 21 coordinate numbers which characterize the geometric configuration of atoms. It can be applied either to molecular moieties or to the macromolecule. Moreover, it allows to calculate parameters not available by analytical techniques. Then a structure is built from the analyses and assumptions defined above, using the software Xmol™ (10). A first step is to construct in a 3D space the molecular moieties, including biomarkers, analyzed as described above: this is done by an editor of molecules which stores these data into a library. Then, starting from the set of equations describing the analytical results and the assumptions, a prediction program selects quantitatively the required cyclic or aliphatic groups from the library and calculates a list of intergroup bonds. Finally, a third program constructs in a 3D space one macromolecule isomer calculated by the prediction program. Although each run of the third program will give one different 3D isomer of the macromolecule, the prediction program has an unique solution for one set of analytical data plus assumptions. It thus allows to characterize the macromolecule by the list of its molecular groups or chemical bonds, whatever the arrangement of molecular groups is.

Among the advantages of this software it allows:
- to list all parameters to be known in order to describe the chemical structure of a given macromolecule,
- to compare the number of assumptions versus analytical data, thus testing the accuracy of the chemical structure,
- to stress some discrepancies among the set of analytical data,
- to take into account, at any time new analytical data which may eliminate assumptions,

- to build self consistent chemical structures which fit all analytical data and to calculate easily the number of each atom or bond.

DISCUSSION

When both kinetic scheme of kerogen cracking and corresponding chemical modelling are achieved, the last problem is to link the two fields of research. The aims of this remaining work are to check, for reference samples, the validity of the kinetic scheme by chemical constraints and then to help to predict thermal cracking of an unknown sample according to its chemical structure, without starting again a complete experimental study. Xmol allows us to describe kerogen or related compounds as a set of chemical bonds or molecular groups, for instance:

a - number of methyl groups,
b - number of ethyl groups,
c - number of aliphatic chains from C3 to C5,
d - number of aliphatic chains from C6 to C13,
e - number of aliphatic chains C14+,
f - number of functional groups such as carbonyl, carboxyl, phenols, alcohols methoxy groups and other ethers,
g - distribution and amount of naphthenic rings,
h - distribution and amount of naphthenoaromatic rings,
i - distribution and amount of aromatic rings.

Each of these molecular groups can be considered as individual and independent reactant during kerogen cracking. Thus, when a given molecular group is considered in the general kinetic scheme described above, knowing its initial proportion in the kerogen structure is enough to predict either its contribution among pyrolysis products derived from kerogen cracking or the proportion of pyrolysis products when it is degraded. Moreover, as the main difference between kerogen types relies on their relative amounts of the same molecular groups, an unified kinetic model for cracking of kerogen could be established. It means that Xmol allows first to choose chemical classes to be taken into account in the kinetic scheme, secondly to know the chemical composition of the C14+ fraction defined in reaction 1 and finally to constrain stoichiometric coefficients of reactions from 1 to 9. For instance:
- total aliphatic carbon content included in methane, ethane, C3-C5 compounds, C6-C13 saturates and C14+ saturates must not exceed the aliphatic carbon content of the initial sample,
- oxygen content included in CO_2, H_2O and coke must not exceed the oxygen content in the initial sample,
- oxygen content included in CO_2 must not exceed the oxygen content included in both carbonyl and carboxyl functional groups,

CONCLUSION

We have checked the feasibility of this new approach for relating thermal reactivity and chemical structure of kerogen only from a qualitative point of view. In the future, we have to confirm this feasibility with quantitative data. Moreover, we need to improve our knowledge of the chemical structure of kerogen, especially on the quantitative determination of functional groups, in order to relate a given functional

group to the yield of non hydrocarbon species released during pyrolysis of kerogen (reactions 1 and 2). Finally, specific and more precise additional analyses can be performed on asphaltenes, such as liquid ^{13}C NMR and some chemical degradation techniques, which could better constraint structural parameters and thus kinetic scheme. Nevertheless, use of Xmol must be considered at its current stage of development mainly as an useful guide for writing kinetic equations but not as a predictive tool i.e. as a substitute of experimental work. The very first use of this software is to give a chemical model of an unknown sample which, up to now, has been considered as a "black box". Even if it is only a model which will certainly be modified in the future according to new analytical data, it allows to set up appropriate experimental work for kinetic studies as well for temperature and time conditions as for analytical procedure for identification and quantification of pyrolysis products.

A direct application of that work extended to complex products such as resins or asphaltenes could be in refinery processes, for thermal treatment of heavy ends of petroleum. This work allows also to link two fields of research, structure of kerogens (and related compounds) and kinetics, which are generally studied by separate research teams.

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Table 1: Chemical composition (wt%) of Boscan 300+, Pematang 340+ and corresponding distillates.

Sample	C6-C13 SAT.	C6-C13 ARO.	C14+ SAT.	C14+ ARO.	RES.	ASP.	H	C	Distillate
Boscan 300+	0	0	13	37	33	17	10,1	82,4	
Boscan 300-	44	20	20	17	0	0	12,9	87,1	10
Pematang 340+	0	0	59	17	23	1	1,8	86,7	
Pematang 340-	57	7	30	6	0	0	14,3	85,7	37

Table 2: Elemental analysis of the two reference kerogens (wt%)

Sample	C	H	N	O	S org.	Pyrite
Type II	55,34	5,85	1,77	10,7	3,46	22,9
Type III	72,86	5,27	1,86	15,9	1,06	3,08

Table 3: Pyrolysis conditions for experimental simulation of kerogen and oil cracking

Sample	Temperature (°C)	Time (h)	Number of experiments
Type II kerogen	260-500	0,5-1900	70
Type III kerogen	250-500	0,5-1900	50
2 oils	350-500	0,5-1000	60
2 distillates	380-500	0,5-1000	65

Table 4: Mass balances (wt%) obtained for Type II kerogen at 300°C for various heatin times

Time (h)	CO_2	H_2O	H_2S	C1	C2-C5	C6-C13 SAT.	C6-C13 ARO.	C14+ extract	Residue
1	2,0	1,7	0,4	0,0	0,2	0,1	0,0	8,5	86,9
9	3,4	2,4	0,7	0,4	0,3	0,3	0,1	17,3	75,1
24	4,0	2,8	0,8	0,5	0,4	0,6	0,2	24,2	66,0
240	4,6	4,2	1,9	0,7	3,0	2,7	1,5	31,1	50,0
648	5,1	4,9	2,3	1,2	3,5	3,7	1,6	26,7	51,0
1296	6,0	4,9	2,5	1,5	4,0	3,9	1,7	26,4	49,0

Table 5 : Analytical data needed for kerogen modelling

ANALYTICAL TECHNIQUE	RESULTS
ATOMIC INFORMATION	
Elemental analysis	Number of atoms (C.H.O.N.S.)
	Amount of Csp^2 bonded to : - 3 CARBONS - 2 CARBONS and 1 HYDROGEN - 1 OXYGEN or NITROGEN by a single bond
I.R. Spectroscopy + ^{13}C NMR	- 1 OXYGEN by a double bond Amount of Csp3 bounded to : - Only CARBON and HYDROGEN - 1 OXYGEN by a single bond - 2 OXYGENS by single bonds
Functional-group analysis	Distribution of functional groups
Pycnometer	Density
MOLECULAR INFORMATION	
	Histogram of CARBON NUMBERS in ALIPHATIC CHAINS
Pyrolysis + Gas chromatography + Mass spectrometry	Histogram of NUMBER of RINGS in CYCLOALKANES Histogram of NUMBER of RINGS in AROMATICS and NAPHTHENOAROMATICS

Csp^2 is a carbon atom with sp^2 hybridization (i.e. aromatic or double bonded). Csp^3 a carbon atom with sp^3 hybridization (i.e. naphthenic or aliphatic).

Table 6 : Hypotheses done for kerogen modelling

Only the elements C, H.O. N, S.
List of molecular groups included in a library
List of possible intergroup bonds (only covalent bonds)
List of possible functional groups and heteroatoms
Elimination of improbable configurations (i.e. a carbon linked to 3 or 4 oxygens)
Number of carbon atoms in the model
Assumptions which supplement analyses (i.e. : percentage of ether linked to 2 aromatic carbons or 2 aliphatic carbons or 1 aromatic and 1 aliphatic carbon)